Heat and Thermal Energy:

Internal energy: U

the energy of a stationary system (when its center of mass is at rest). This includes **potential energy** (compressed spring), nuclear or chemical **binding energy**, **internal kinetic energy** (linear motion of molecules, but also vibration or rotation), etc.

Thermal energy:

the portion of internal energy **depending on temperature**.

Heat: Q

Transfer of thermal energy from one system to another (which are at different temperatures).

Units of heat: Joule, cal, kcal, btu. 1 cal=4.186 J.

Heat (Q) is similar to **work (W)**. You consume energy to do work. In the same manner, it takes energy to heat up another system.

Calorimetry Problems:

Use units consistently. In physics, use kg, J, and degrees K or C. In chemistry or engineering, other units may be more customary.

Does a body gain or lose heat ? Check your signs.

Which terms describe the gain or loss of heat? Include terms for specific heat for the solid, liquid, and gas phase, and the heat of fusion and vaporization (if applicable).

First Law of Thermodynamics:

The internal energy of a system changes when work is done on the system (or by it), and when it exchanges heat with the environment:

$$\Delta U = U_f - U_i = Q - W$$

Sign convention:

Work (W) done **by** the system is **positive**, work done **to** the system is **negative**. Heat (Q) absorbed by the system (leading to an increase in internal energy) is positive, heat released to the environment is negative.

Applications of the First Law of Thermodynamics:

Q and W depend on the path taken, but P, V, T, and U do not depend on the path (state variables or state functions). Therefore, Q and W are not properties of the system, but rather properties of the process.

Isothermal process:
The system expands (or contracts) at constant temperature. Therefore, it absorbs (or releases) heat from (to) its environment.

$$\Delta U=0 \quad \text{or} \quad Q=W.$$

For an ideal gas, we have

$$PV=nRT,$$

and therefore

$$W=nRT\ln(V_f/V_i).$$

Isobaric process:
happens at constant pressure, therefore

$$W=P\Delta V.$$

Isovolumetric process:
happens at constant volume, therefore

$$W=0.$$

<u>Quasistatic process:</u>
The process is very slow, the system is always in thermal equilibrium.

<u>Adiabatic process:</u>
The system is **isolated** and therefore does not exchange heat with its environment during the expansion/contraction.

$$Q=0 \quad \text{or} \quad \Delta U=W.$$

<u>Cyclic process:</u>
The process originates and ends at the same state.
Example: heat engines.

$$\Delta U=0,\ Q=W$$

<u>Adiabatic free expansion:</u> **W=0, Q=0.**

Three laws of Thermodynamics:

Thermodynamics is like statistics in a casino:

1. You can't win.

2. You can't break even.

3. You can't even get close.

<u>Second Law of Thermodynamics:</u>

Some processes are **<u>irreversible</u>**:

1. When two objects at different temperatures are placed in thermal contact with each other, thermal energy always flows from the warmer to the cooler object, never from the cooler to the warmer.

2. A rubber ball dropped to the ground bounces several times and eventually comes to rest, but a ball lying on the ground never begins bouncing on its own.

3. An oscillating pendulum eventually comes to rest because of collisions with air molecules and friction at the point of suspension, and the initial mechanical energy is converted to thermal energy; the reverse conversion of energy never occurs.

All these processes are irreversible. The reverse process could happen according to the first law of thermodynamics, but is **forbidden by the second law** .

Heat engines

Heat engines are driven by a cyclic process, there the internal energy of the engine remains constant from one cycle to the next:

$$\Delta U=0.$$

Therefore, by the First law, the heat absorbed by the engine (heat supplied by the fuel Q_h minus heat released via the exhaust system Q_c) is equal to the work down by the system:

$$Q_h-Q_c=W.$$

The thermal efficiency e of a process is the work done divided by the fuel used:

$$e=\frac{W}{Q_h}=\frac{Q_h-Q_c}{Q_h}=1-\frac{Q_c}{Q_h}<1.$$

Second Law of Thermodynamics:

All heat engines have an efficiency smaller than 1.

Every heat engine releases some heat (through the exhaust system) to the cold reservoir.